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A New Method for the Synthesis of Polymers Containing Amide and Imide Groups in the Main Chain

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SUMMARY:

Poly(pyromellitdiimidoarylenecarbonyliminoaryleneiminocarbonylarylene)s [poly(amide-imide)s] (**7** and **12**) were prepared from pyromellitic dianhydride (**6**) and dicarbamates (**5**) (diurethanes) containing amide linkages. The same polymers could also be prepared directly from aromatic isocyanatocarboxylic acid chlorides (**10**), diamines (**11**) and **6**. In the latter method, the addition of an equimolar amount of water was required for the formation of the imide ring in the main chain of the polymer. Model reactions were carried out to determine the reaction conditions for the two methods. Reaction mechanisms are proposed.

ZUSAMMENFASSUNG:

Aus Pyromellitsäuredianhydrid (**6**) und Dicarbamaten (**5**) (Diurethanen), die Amidbindungen enthalten, wurden Poly(pyromellitdiimidoarylencarbonyliminoaryleniminocarbonylarylen)e [Poly(amid-imid)e] (**7** und **12**) hergestellt. Dieselben Polymeren konnten auch direkt aus aromatischen Isocyanatocarbonsäurechloriden (**10**), Diaminen (**11**) und **6** hergestellt werden. Im letzteren Fall war eine äquimolare Menge Wasser für die Bildung des Imidringes in der Polymerhauptkette erforderlich. Durch Modellreaktionen wurden die Reaktionsbedingungen für beide Methoden bestimmt und Reaktionsmechanismen vorgeschlagen.

Introduction

It has been reported that amines react preferentially with the acid chloride group of aromatic isocyanatocarboxylic acid chlorides (**10**) to give amide derivatives containing the isocyanate group, whereas ethanol reacts with the isocyanate group of aromatic isocyanatocarboxylic acid chlorides (**10**) to give carbamate (urethane) derivatives containing the acid chloride group[1,2]. In a previous paper, it has been shown that phenol also reacted at the isocyanate site of *p*-isocyanatobenzoyl chloride to yield an urethane derivative. From this product, diurethanes containing the amide linkage were prepared by condensing it with diamines. The synthesis of poly(amide-quinazolinedione)s from these compounds has already been reported[3]. In this case, it has been shown that diurethane was converted to diisocyanate at elevated temperature which in its turn reacted with bis(*o*-amino ester) to produce the polymer.

In several recent reports, diisocyanates have been used for the preparation of polyimides by heating them with aromatic dianhydrides[4-6]. By the same method, polymers containing amide and imide groups in the main chain, in the following text called poly(amide-imide)s, have been prepared from diisocyanates and trimellitic acid anhydride[7-9].

The present paper reports the preparation of poly(amide-imide)s starting from aromatic isocyanatocarboxylic acid chlorides (**10**) or more indirectly from diurethanes containing the amide linkage.

Results and Discussion

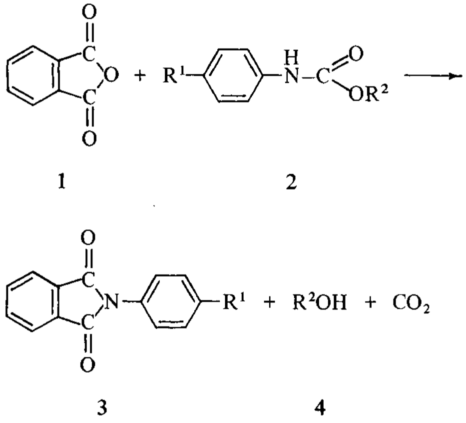
Poly(amide-imide)s from diurethanes containing the amide linkage

Reaction of urethanes with phthalic anhydride

It has been reported that *N*-phenylphthalimide (**3a**) can be obtained in rather high yield by heating a mixture of phenyl isocyanate and phthalic anhydride (**1**) at elevated temperature[10]. From this reaction, *Meyers*[4] prepared polyimide from pyromellitic dianhydride (**6**) and bis(4-isocyanatophenyl)methane. Recently, *Carleton* et al.[5,6] also prepared polyimides based on this reaction and they found that water and ethanol accelerated the rate of formation of **3a** in the model reaction. Water may cause the hydrolysis of isocyanate to the amine or to the corresponding urea derivative which reacts with anhydride at elevated temperature to give an imide, whereas the amine adds to the anhydride giving an amide acid which by dehydration is converted to an imide. Ethanol, however first reacts with isocyanate to form a urethane which by reacting with anhydride is converted slowly to an imide with the formation of CO_2 and ethanol. The cycle is repeated until isocyanate is completely consumed.

In a previous communication, we have shown that urethanes react with epoxides in the presence of tertiary amine as catalyst to give oxazolidones in high yields[11]. On extending this reaction to difunctional monomers, polymers containing the oxazolidone units in the main chain have been prepared[12].

In subsequent investigations, the reaction of urethanes with **1** was studied (Eq. (i)).



(i)

2, 4	a	b	c
R^1	H	H	C_6H_5NHCO
R^2	CH_3CH_2	C_6H_5	C_6H_5

3	a	b
R^1	H	C_6H_5NHCO

A solution of urethane and **1** was slowly heated up to the reflux temperature of the solvent. The reaction was considered to be complete when no further carbon dioxide evolved. In most solvents, the evolution of carbon dioxide was observed at a temperature of $\approx 30\,^{\circ}C$. The resulting *N*-phenylphthalimide (**3a**) was identified by its melting point and IR spectrum. The results carried out in various solvents are summarized in Tab. 1.

From this, it was found that:

(A) The yield of imide was high when the reaction was carried out in inert polar solvents such as *N*-methyl-2-pyrrolidone (NMP).

(B) The yield was low in polar solvents which are known to react with isocyanates at elevated temperatures. *N*,*N*-Dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc) and hexamethyl phosphoric acid triamide (HMPT)

Tab. 1. Effect of solvent on the yield of *N*-phenylphthalimide (**3a**) prepared from phthalic anhydride (**1**) and *N*-phenylurethanes (**2a** and **2b**)

Solvent[a]	From **2a**		From **2b**	
	time in h	% yield	time in h	% yield
NMP	5	73	3	80
DMAc	4	12	4	73
DMF	5	0	3	67
HMPT	4	0	4	0
Pyridine	24	21	24	84
Diglyme	32	26	12	74
Toluene	60	0	60	12

[a] NMP: *N*-methyl-2-pyrrolidone; DMAc: *N*,*N*-dimethylacetamide; DMF: *N*,*N*-dimethylformamide; HMPT: hexamethyl phosphoric acid triamide; Diglyme: 2,5,8-Trioxanonane.

are examples. No imide was obtained in the case of HMPT used as solvent, although a violent evolution of CO_2 was observed.

(C) The yield was low in nonpolar solvents such as toluene even at long reaction times.

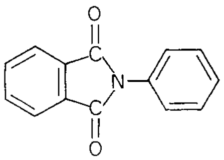
(D) *O*-phenylurethane gave a higher yield of imide than *O*-ethylurethane in all the solvents used.

In addition, the reaction was not catalyzed by tertiary amines such as triethylamine or 1,4-diazabicyclo[2.2.2]octane (triethylenediamine).

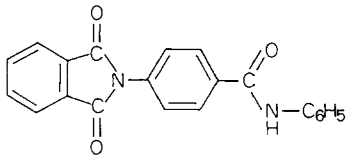
From the above results, the reaction of urethanes with **1** to produce the imide **3a** was considered to follow two pathways. One of these is that urethanes may react directly with anhydride to yield imide as suggested by *Carleton* et al.[5]. The other one is the decomposition of urethanes by heating into phenol or ethanol and isocyanates which react with anhydride to produce imide. However, the second pathway was thought to be the major one. This speculation was supported by the fact that *O*-phenylurethane decomposes into isocyanate more easily than *O*-ethylurethane[13] and that the reaction was not catalyzed by amines, whereas urethane reacts directly with electrophilic reagents via an adduct intermediate[11].

Preparation of poly(amide-imide)s from diurethanes

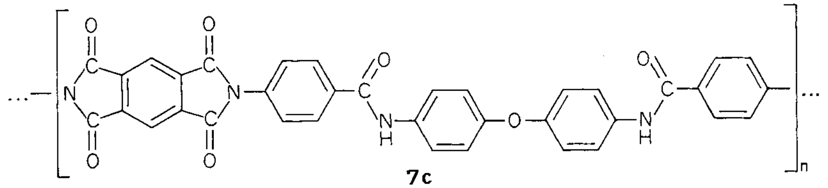
In order to confirm the structure of the resulting polymers, the reaction between phenyl *N*-(4-phenylaminocarbonylphenyl)carbamate (**2c**) and **1** was



3a



3b



7c

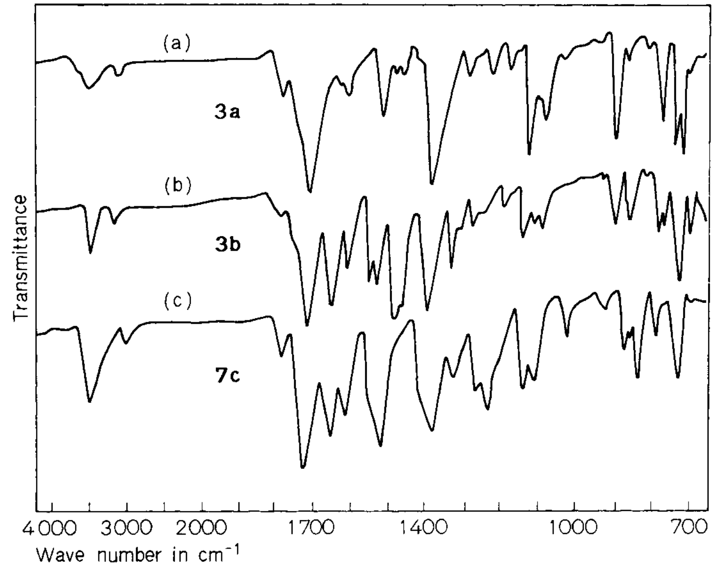
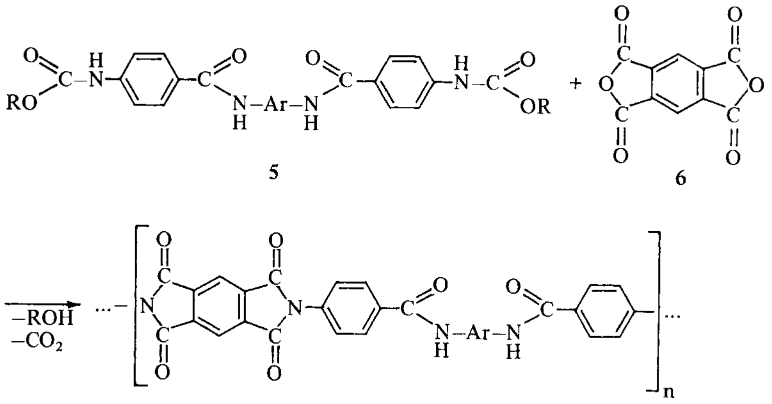


Fig. 1. IR spectra (KBr) of (a): *N*-phenylphthalimide (**3a**), (b): 4-phthalimidobenzanilide (**3b**), and (c): poly(amide-imide) **7c**

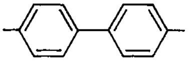
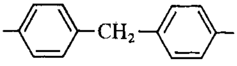
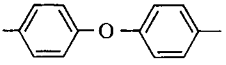
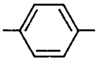
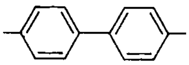
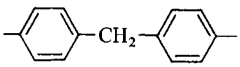
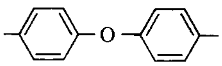
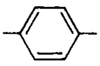
carried out in NMP. Fig. 1 (b) shows the IR spectrum of the product, 4-phthalimidobenzanilide (**3b**).

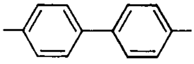
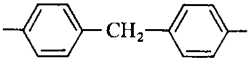
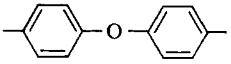
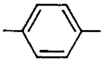
The amide absorption bands at 1650 cm^{-1}, the imide carbonyl bands at 1790 and 1720 cm^{-1}, and the absorption at 720 cm^{-1}, characteristic of the imide ring, were observed. The structure of **3b** was also supported by elemental analysis.

By extending this reaction to difunctional monomers, poly(pyromellitdiimido-1,4-phenylenecarbonylimino-1,4-aryleneiminocarbonyl-1,4-phenyle-



7

5	R	Ar
a	C_6H_5	
b	C_6H_5	
c	C_6H_5	
d	C_6H_5	
e	CH_3CH_2	
f	CH_3CH_2	
g	CH_3CH_2	
h	CH_3CH_2	

7	Ar
a	
b	
c	
d	

ne)s*) [poly(amide-imide)s] (**7**) were obtained from diurethanes (**5**) containing amide linkages and pyromellitic dianhydride (**6**) (Eq. (ii)).

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*) Nomenclature: IUPAC Information Bulletin No. 29, 1972; J. Polym. Sci. Part B, **11**, 389 (1973).

The polycondensation was performed by heating slowly a mixture of **5** and **6** in NMP up to 210 °C. The reaction was stopped after 2–4 h when no further CO_2 was formed. The results are listed in Tab. 2.

Tab. 2. Poly(amide-imide)s **7** from diurethanes **5** and pyromellitic dianhydride (**6**)

Polymer	Prepared from **5a–d**		Prepared from **5e–h**	
	% yield	η_{inh}[a]	% yield	η_{inh}[a]
7a	96	0,58	94	0,15
7b	96	0,38	88	0,16
7c	98	0,40	47	0,12
7d	92	0,35	54	0,11

[a] $c = 0{,}5\ g/100\ cm^3$ of conc. H_2SO_4 at 30 °C.

Tab. 3. Dissociation temperatures of diurethanes **5a–h**[a]

Diurethanes 5	**a**	**b**	**c**	**d**
Dissociation temp. in °C	222–331	212–308	210–295	215–325

Diurethanes 5	**e**	**f**	**g**	**h**
Dissociation temp. in °C	250–344	230–320	247–312	280–354

[a] The temp. at which diurethanes dissociated into isocyanate and phenol or ethanol was measured by differential and thermogravimetric analysis; heating rate: 5 °C/min in air.

As in the case of the reaction of **2** with **1**, the elimination of CO_2 began at 30 °C up to the reflux temperature of NMP. As the dissociation of diurethanes occurred at temperatures >200 °C (Tab. 3), the reaction between **5** and **6** to produce poly(amide-imide)s **7** might also follow two pathways as mentioned above. However, the major pathway for the formation of polymers was considered to be the reaction between diisocyanates generated from **5** and **6** based on the yields and viscosities of the resulting polymers. As shown in Tab. 2, bis(*O*-phenylurethane)s gave polymers of higher yield and higher viscosity than those of bis(*O*-ethylurethane)s.

Poly(amide-imide)s (**12**) from aromatic isocyanatocarboxylic acid chlorides (**10**)

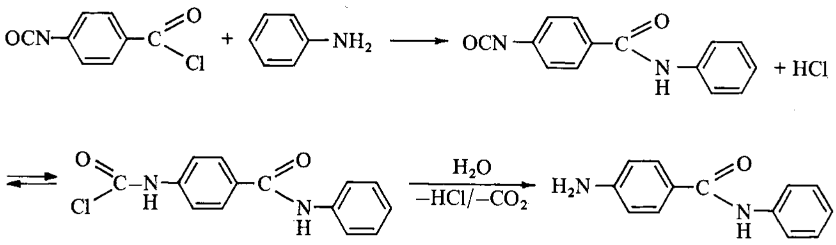
As mentioned in the Introduction, amines have been reported to react preferentially with the acid chloride group of aromatic isocyanatocarboxylic acid chlorides. It was, therefore, decided to prepare poly(amide-imide)s directly from these compounds by the following polymerization process. First, by reacting 2 mol of isocyanatocarboxylic acid chloride (**10**) with 1 mol of diamine **11**, the diisocyanate containing the amide linkage was formed. This product was then allowed to condense with **6** to give the poly(amide-imide) **12** (Eq. (iv)).

At first, the suitable conditions for the preparation of polymers were determined by a model reaction. For this, a solution of aniline in NMP was added slowly to an equimolar solution of *p*-isocyanatobenzoyl chloride at −18 °C and the reaction temperature was slowly raised to room temperature. Then **1** was added and the temperature was gradually raised to 200 °C. Against expectation, no imide was isolated from the reaction mixture, although, the liberation of CO_2 was observed during the course of the reaction.

However, when the reaction was carried out under the same conditions but in the presence of an equimolar amount of water, 4-phthalimidobenzanilide (**3b**) was obtained in good yield.

The comparison of the IR spectra and the elemental analysis supported the structure. The addition of water to the reaction mixture caused a violent elimination of CO_2 already at room temperature, and the reaction slowed down when the temperature was gradually raised.

Based on this observation and on the fact that NMP is a solvent of relatively weak basicity, it was assumed that carbamoyl chloride **8** was formed by

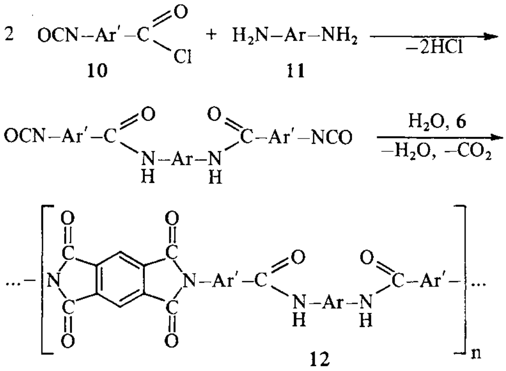


8

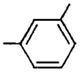
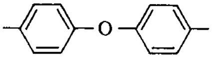
9

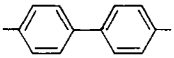
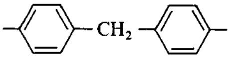
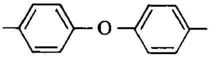
(iii)

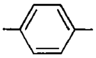
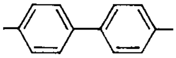
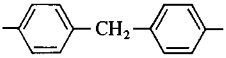
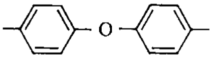
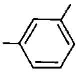
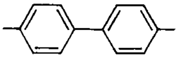
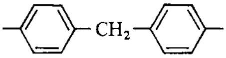
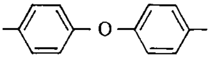
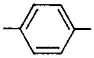
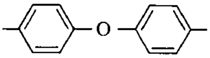
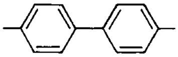
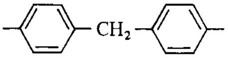
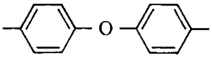
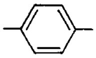
$$9 \xrightarrow[-H_2O]{1} 3b$$



(iv)

10	Ar′
a	
b	
c	

11	Ar
a	
b	
c	
d	

12	Ar′	Ar
a		
b		
c		
d		
e		
f		
g		
h		
i		
j		
k		
l		

addition of the generated hydrogen chloride to the unreacted isocyanate group as shown in Eq. (iii). However, in a side reaction, **8** could decompose into isocyanate at elevated temperature which then reacts with **1** to form **3b** and CO_2. By addition of water (Eq. (iii)) an unstable carbamic acid is formed which loses CO_2 to give the amine derivative **9** which condenses with **1**, to produce the imide **3b**. **9** could also react with **8** to form the corresponding urea which then condenses with **1** to give imide **3b** as the final product[6]. The pathway of the model reaction, therefore, was not so simple as illustrated in Eq. (iii).

Thus, the polycondensation was carried out in NMP under the same conditions as the model reaction. Diamine **11** was first allowed to react with isocyanatocarboxylic acid chloride **10** followed by the addition of **6** and water (Eq. (iv)).

The results obtained by this method are summarized in Tab. 4. Compared with the results obtained from diurethanes **5**, this direct method gave polymers of slightly higher molecular weight. These polymers **12** were insoluble in

Tab. 4. Poly(amide-imide)s **12** from isocyanatocarboxylic acid chlorides **10**, diamines **11**, and pyromellitic dianhydride (**6**)

Polymer **12**	% Yield[a]	η_{inh}[b]	$T_{dec.}$[c] in °C
a	90	0,47	435
b	q.	0,31	420
c	99	0,54	456
d	95	0,33	440
e	93	0,33	430
f	q.	0,21	420
g	q.	0,19	426
h	90	0,29	429
i	q.	0,63	468
j	q.	0,76	423
k	q.	0,66	432
l	95	0,74	444

[a] q. = quantitative.

[b] 0,5 g/100 cm³ of conc. H_2SO_4 at 30 °C.

[c] $T_{dec.}$: The temp. at which the initial weight loss of the polymer occurred in thermogravimetric analysis; heating rate: 10 °C/min in nitrogen atmosphere.

common organic solvents, but soluble in methanesulfonic acid and conc. sulfuric acid.

The thermogravimetric analysis indicated that poly(amide-imide)s were stable in nitrogen atmosphere up to about 440 °C (Fig. 2 and Tab. 4).

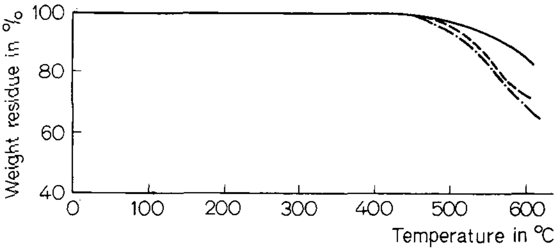


Fig. 2. Thermogravimetric analysis curves of poly(amide-imide)s; heating rate: 10 °C/min in nitrogen atmosphere. (——): **12c**; (– – –): **12e**; (–·–·): **12j**

Experimental Part

All solvents were purified by the usual procedure.

Materials: Phenyl *N*-phenylcarbamate (**2b**) was prepared from phenyl isocyanate and phenol with triethylamine as a catalyst. Ethyl *N*-phenylcarbamate (**2a**) was obtained commercially and used without further purification. 3- and 4-isocyanatobenzoyl chlorides and 4-(4-isocyanatophenoxy)benzoyl chloride (**10c**) were prepared by treating the corresponding aminocarboxylic acids with phosgene and phosphorus pentachloride in dioxane[2,14]. Diurethanes containing the amide linkage were prepared according to the method described in a previous paper[3]. Phthalic anhydride (**1**) and pyromellitic dianhydride (**6**) were commercially available and used without further purification.

Preparation of N-phenylphthalimide (**3a**) *from phenyl N-phenylcarbamate* (**2b**) *and phthalic anhydride* (**1**): A mixture of 1,48 g (0,010 mol) of **1** and 2,13 g (0,010 mol) of **2b** in 20 ml of *N*-methyl-2-pyrrolidone (NMP) was heated slowly to 210 °C for 3 h. After cooling, the reaction mixture was poured into ethanol to precipitate the product. Yield: 1,77 g (80%). Colorless needles (from ethanol); mp 204–206 °C (lit.[10]: mp 204–205 °C).

$C_{14}H_9NO_2$ (223,2)	Calc.	C 75,32	H 4,06	N 6,28
	Found	C 75,51	H 3,80	N 6,31

Preparation of 4-phthalimidobenzanilide (**3b**) *from phenyl N-(4-phenylaminocarbonylphenyl)carbamate* (**2c**) *and phthalic anhydride* (**1**): A mixture 0,444 g (0,003 mol) of **1** and 0,996 g (0,003 mol) of (**2c**) in 10 ml of NMP was heated at 210 °C during 3 h. The product was isolated by pouring the reaction mixture into methanol. Yield: 0,864 g (84%); mp 308–310 °C (from acetic acid).

$C_{21}H_{14}N_2O_3$ (342,3)	Calc.	C 73,67	H 4,12	N 8,18
	Found	C 72,95	H 3,66	N 7,80

Preparation of 4-phthalimidobenzanilide (**3b**) *from 4-isocyanatobenzoyl chloride* (**10a**), *aniline, and* **1**: To a solution of 1,82 g (0,010 mol) of **10a** in 20 ml of NMP at −18 °C, a solution of 0,93 g (0,010 mol) of aniline in 20 ml of NMP was added slowly over a period of 1 h. After 1 h at −15 to 0 °C and 2 h at room temp. 1,48 g (0,010 mol) of **1**, followed by 0,18 g (0,010 mol) of water was added. After stirring at room temp. for 1 h, the temp. was slowly raised to 200 °C for 3 h. The product was precipitated in methanol. Yield: 2,44 g (84%). Colorless powder; mp 308–309 °C (from acetic acid).

$C_{21}H_{14}N_2O_3$ (342,3)	Calc.	C 73,67	H 4,12	N 8,18
	Found	C 73,05	H 3,46	N 7,82

Preparation of poly(pyromellitdiimino-1,4-phenylenecarbonylimino-1,4-phenylenemethylene-1,4-phenyleneiminocarbonyl-1,4-phenylene), [poly(amide-imide)] (**7b**), *from diurethane* **5b** *and pyromellitic dianhydride* (**6**): A mixture of 1,014 g (0,0015 mol) of **5b** and 0,327 g (0,0015 mol) of **6** in 20 ml of NMP was heated to 210 °C for 4 h. The polymer was precipitated in acetone, washed with acetone and dried i. vac. at 100 °C. Yield: 0,893 g (96%), η_{inh}: 0,38 (0,5 g/100 ml in H_2SO_4, 30 °C .

$(C_{37}H_{22}N_4O_6)_n$ $(618{,}6)_n$	Calc.	C 71,84	H 3,56	N 9,06
	Found	C 70,81	H 3,91	N 8,58

The poly(amide-imide)s **7a, c** and **d** were prepared analogously from the corresponding diurethanes. Yields and η_{inh} are summarized in Tab. 2.

Preparation of poly(pyromellitdiimino-1,4-phenylenecarbonylimino-1,4-phenyleneoxy-1,4-phenyleneiminocarbonyl-1,4-phenylene), [poly(amide-imide)] (**12c**), *from 4-isocyanatobenzoyl chloride* (**10a**), *bis(4-aminophenyl) ether* (**11c**), *and pyromellitic dianhydride* (**6**): To a solution of 1,82 g (0,010 mol) of **10a** in 20 ml of NMP at −18 °C, a solution of 1,00 g (0,005 mol) of **11c** in 20 ml of NMP was added dropwise over a period of 70 min. After 2 h at −10 to 5 °C and 2 h at room temp., 1,09 g (0,005 mol) of **6**, followed by 0,18 g of water, were added. The mixture was stirred at room temp. for 1 h and then heated at 200 °C for 2 h. After cooling, it was poured into acetone, washed repeatedly with acetone and dried. Yield: 3,07 g (99%); η_{inh}: 0,54 (0,5 g/100 ml in H_2SO_4, 30 °C).

$(C_{36}H_{20}N_4O_7)_n$ $(620{,}5)_n$	Calc.	C 69,68	H 3,23	N 9,03
	Found	C 67,46	H 3,39	N 8,85

The poly(amide-imide)s **12a, b, d–l** were prepared analogously from the corresponding isocyanatocarboxylic acids **10** and the diamines **11**. Yields and η_{inh} are summarized in Tab. 4.

[1] Y. Iwakura, K. Uno, S. Kang, J. Org. Chem. **31**, 142 (1966)
[2] S. Kang, Dissertation, University of Tokyo 1965
[3] Y. Iwakura, K. Uno, N. Chau, Polym. J. **5**, 301 (1973)
[4] R. A. Meyers, J. Polym. Sci. Part A-1, **7**, 2757 (1969)
[5] W. J. Farrissey, J. S. Rose, P. S. Carleton, J. Appl. Polym. Sci. **14**, 1093 (1970)
[6] P. S. Carleton, W. J. Farrissey, J. S. Rose, J. Appl. Polym. Sci. **16**, 2983 (1972)

7) M. Nakano, G. Koyama, Preprints 19th Ann. Meeting Polymer Soc. Japan **1,** 126 (1970)

8) S. Terney, J. Keating, J. Zielinski, J. Hakala, H. Sheffer, J. Polym. Sci. Part A-1, **8,** 683 (1970)

9) Y. Imai, T. Takahashi, Kobunshi Kagaku [Chem. High Polymers (Tokyo)] **29,** 182 (1972)

10) C. D. Hurd, A. G. Prapas, J. Org. Chem. **24,** 338 (1959)

11) Y. Iwakura, S. Izawa, J. Org. Chem. **29,** 379 (1964)

12) Y. Iwakura, S. Izawa, F. Hayano, J. Polym. Sci. Part A-1, **4,** 751 (1966)

13) J. H. Saunders, K. C. Frisch, "Polyurethanes, Chemistry and Technology, Part 1: Chemistry", Interscience Publ., New York 1962, p. 108

14) Y. Iwakura, K. Uno, N. Chau, Makromol. Chem. **175,** 2079 (1974)